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Thermal Decomposition of Specifically Phosphorylated D-Glucoses and Their Role in the Control of the Maillard Reaction

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One of the main shortcomings of the information available on the Maillard reaction is the lack of knowledge to control the different pathways, especially when it is desired to direct the reaction away from the formation of carcinogenic and other toxic substances to more aroma and color generation. The use of specifically phosphorylated sugars may impart some elements of control over the aroma profile generated by the Maillard reaction. Thermal decomposition of 1- and 6-phosphorylated glucoses was studied in the presence and absence of ammonia and selected amino acids through pyrolysis/gas chromatography/mass spectrometry using nonpolar PLOT and medium polar DB-1 columns. The analysis of the data has indicated that glucose-1-phosphate relative to glucose undergoes more extensive phosphate-catalyzed ring opening followed by formation of sugar-derived reactive intermediates as was indicated by a 9-fold increase in the amount of trimethylpyrazine and a 5-fold increase in the amount of 2,3-dimethylpyrazine, when pyrolyzed in the presence of glycine. In addition, glucose-1-phosphate alone generated a 6-fold excess of acetol as compared to glucose. On the other hand, glucose-6-phosphate enhanced retro-aldol reactions initiated from a C-6 hydroxyl group and increased the subsequent formation of furfural and 4-cyclopentene-1,3-dione. Furthermore, it also stabilized 1- and 3-deoxyglucosone intermediates and enhanced the formation of six carbon atom-containing Maillard products derived directly from them through elimination reactions such as 1,6-dimethyl-2,4-dihydroxy-3-(2H)-furanone (acetylformoin), 2-acetylpyrrole, 5-methylfurfural, 5-hydroxymethylfurfural, and 4-hydroxy-2,5-dimethyl-3-(2H)-furanone (Furaneol), due to the enhanced leaving group ability of the phosphate moiety at the C-6 carbon. However, Maillard products generated through the nucleophilic action of the C-6 hydroxyl group such as 2-acetylfuran and 2,3-dihydro-3,5-dihydroxy-4H-pyran-4-one were retarded, due to the blocked nucleophilic atom at C-6.

KEYWORDS: Maillard reaction; mechanism; glucose-1-phosphate; glucose-6-phosphate; phosphate ions

INTRODUCTION

The Maillard reaction between amino acids and reducing sugars is a major route to flavor and color formation in cooked foods (*1*). The reaction involves complex pathways leading to a wide range of products, including a number of carcinogens (*2*). The reaction has been extensively studied in recent years, mainly through the examination of the products formed in model systems between individual amino acids and sugars and using isotopically labeled reactants (*3*). However, the influence of the specifically phosphorylated sugars on the profile generated through Maillard reaction has not been systematically examined, although their effect on 4-hydroxy-2,5-dimethyl-3-(2H)-furanone (Furaneol) formation has been studied (*4*) and the effect of phosphate buffer has been the subject of a few investigations. Potman and Wijik (*5*) have demonstrated the catalytic role of phosphate ions in accelerating the Amadori rearrangement through general base catalysis at 100 °C in a glycine/glucose model system. Similarly, Bell (*6*) showed that the rate of glycine loss and browning increased with increasing phosphate buffer concentration even at 25 °C over long-term storage. The author has attributed this result to the bifunctional catalytic activity of the phosphate anion. Earlier, Burton and McWeeny (*7*) noted a similar color enhancement in the presence of phosphate buffer during Maillard model studies and attributed this effect to the increased concentration of the open form of glucose in the presence of phosphate ions. The effect of phosphate buffer was also observed on the rate of protein glycation (*8*) and was attributed earlier to the neighboring catalytic effect of phosphate ions (*9*). Specifically phosphorylated sugars such as glucose-1-phosphate or glucose-6-phosphate could influence differently

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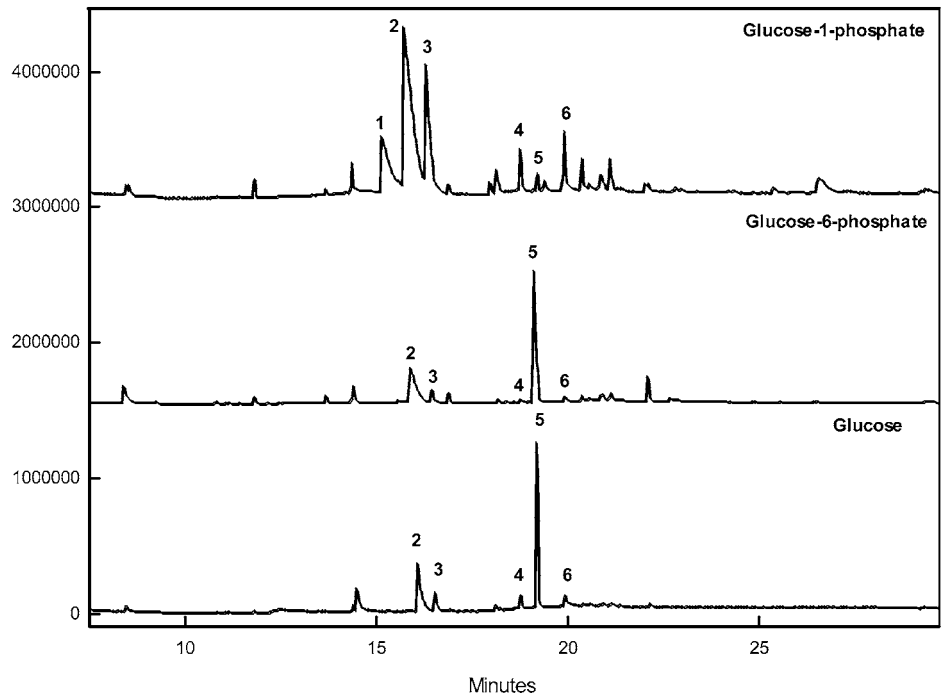


Figure 1. Chromatograms of pyrolysis of glucose, glucose-1-phosphate, and glucose-6-phosphate on a PLOT-Q capillary column. Key: 1, formic acid; 2, acetic acid; 3, acetol; 4, acrylic acid; 5, furfural; 6, 2-furanmethanol.

the course of Maillard reaction relative to free phosphate ions. These sugars are present in food systems in relatively large amounts. For example, glucose concentration in beef was 148 (wet weight) vs 80 mg/100 g of corresponding phosphate sugars, 33 vs 32 mg for fructose, and 26 vs 9 mg/100 g in the case of ribose (*10*). In addition, analysis of chicken breast also indicated the presence of 35.3 mg of glucose vs 13.8 mg of glucose phosphates/100 g of sample and in the chicken leg the amounts were 14.0 vs 8.3 mg/100 g. The addition of sugar phosphates in raw beef caused important changes in terms of quantities of flavor compounds formed. It seemed that ribose-5-phosphate was more reactive than ribose in an aqueous model system and produced more volatile compounds (*10*). Ribose-5-phosphate has been proposed to be the precursor of the important intermediate 4-hydroxy-5-methyl-3-(2H)-furanone, which further reacts to give flavor compounds (*11*). It has been also reported that phosphate buffer salts could act as effective catalysts for the Maillard reaction (*12*). However, the reactivity of phosphate sugars and their further degradation under dry, roastlike conditions have not been reported yet. Investigations of the volatile products of such reactions are not just of interest for the formulation of flavorings but also are important to our understanding of the role played by specifically blocked hydroxyl groups of the sugar, in directing the course of Maillard reaction.

Pyrolysis coupled with gas chromatography/mass spectrometry (Py/GC/MS) has been demonstrated to be a fast and convenient technique for the analysis of Maillard reaction products (*12*). It combines a fast reaction time (20 s) and the use of a small amount of reactants (milligrams) enabling the use of expensive labeled compounds for mechanistic studies. In this study, we have investigated by Py/GC/MS the influence of the phosphate groups on the degradation of phosphorylated glucoses in the presence and absence of selected amino acids.

MATERIALS AND METHODS

D-Glucose and L-cysteine hydrochloride, glycine, and ammonium carbonate were purchased from Aldrich Chemical Co. (Milwaukee, WI); β-D-glucose-6-phosphate monosodium salt, phosphoric acid, and α-D-glucose-1-phosphate disodium salt tetrahydrate were purchased from Sigma Chemical Co. (St. Louis, MO); sodium phosphate dibasic anhydrous (reagent ACS) was purchased from Acros Organics Chemicals (Springfield, NJ).

Py/GC/MS Analysis. All Py/GC/MS analyses were performed using a Hewlett-Packard 5890 series II GC fitted with a 5971B MS (Hewlett-Packard, Palo Alto, CA) and a CDS Pyroprobe 2000 unit interface (CDS Analytical Inc., Oxford, PA). Solid samples of sugar−ammonium carbonate or amino acid mixtures (1:3 ratio, 2 mg), sugar/sodium phosphate dibasic (1:4 ratio, 2 mg), or single compounds were introduced inside a quartz tube (0.3 mm thickness), plugged with quartz wool, and inserted into the coil probe. The pyroprobe was set at 250 °C at a heating rate of 50 °C/ms with a total heating time of 20 s. The pyroprobe interface was set at 250 °C. The samples were introduced in splitless mode and analyzed under pulsed pressure (20 psi for 2 min, drop to 1.6 psi at a rate of 99 psi/min to establish a constant flow of 1.5 mL/min); the pressure was regulated by an electronic pressure controller (Hewlett-Packerd). The capillary direct MS interface temperature was 180 °C; the ion source was 280 °C. The ionization voltage was 70 eV, and the electron multiplier was 2047 V. The MS scanned masses from *m*/*z* 17 to 500 at 1.5 scans/s. For the PLOT-Q capillary column (Hewlett-Packard, Mississagua, ON), the column temperature was held at 20 °C for 2 min, then increased to 100 °C at a rate of 30 °C/min, further increased to 250 °C at a rate of 10 °C/min, and kept at 250 °C for 10 min; for the DB-1 capillary column separations, the column temperature was held at −5 °C for 2 min, then increased to 150 °C at a rate of 10 °C/min, further increased to 250 °C at a rate of 20 °C/min, and kept at 250 °C for 10 min. Compounds were tentatively identified by comparing their mass spectra with those of Wiley and NIST mass spectral databases. The identity and purity of the chromatographic peaks were determined using NIST AMDIS version 2.1 software. The reported formation efficiency values are the average of duplicate analyses and are rounded off, with no more than 6% relative error in reproducibility.

RESULTS AND DISCUSSION

Although the Maillard reaction has been studied in detail, one of the main shortcomings of the available information is the lack of knowledge that allows the researchers to control the different pathways, especially when it is desired to direct the reaction away from formation of carcinogenic and other toxic

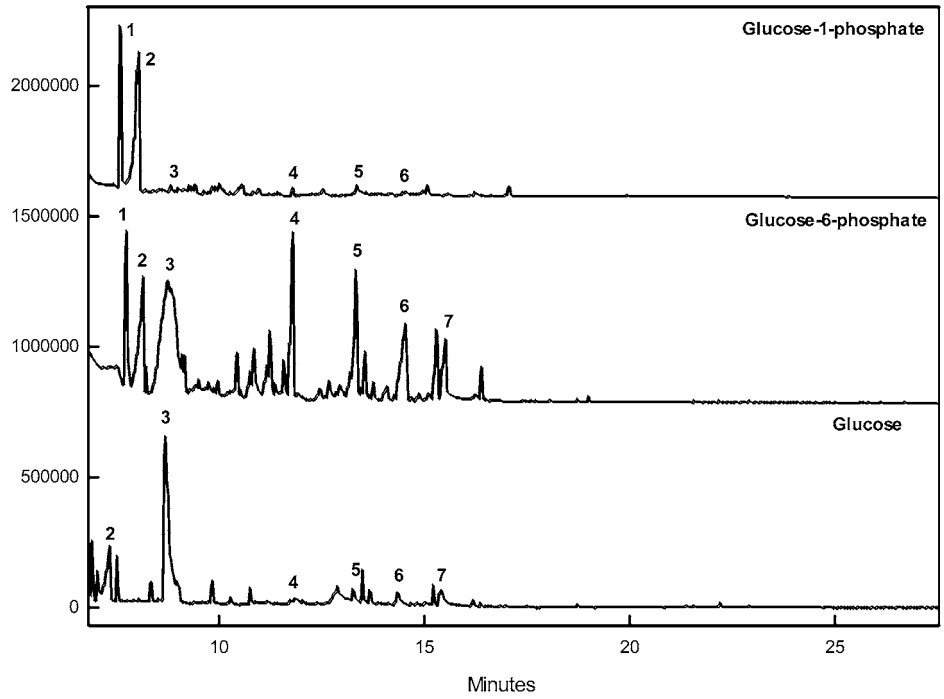


Figure 2. Chromatograms of pyrolysis of glucose, glucose-1-phosphate, and glucose-6-phosphate on a DB-1 capillary column. Key: 1, formic acid; 2, acetic acid; 3, furfural; 4, 1,6-dimethyl-2,4-dihydroxy-3-(2H)-furanone (acetylformoin); 5, 4-hydroxy-2,5-dimethyl-3-(2H)-furanone (Furaneol); 6, pyranone; 7, HMF.

Table 1. Formation Efficiencies[a] ($\times 10^{12}$) of Selected Pyrolysis Products of Glucose-1-phosphate (gl1p), Glucose-6-phosphate (gl6p), and Glucose (gl) on a PLOT-Q Capillary Column

	name	t_R (min)	gl1p	gl6p	gl
1	formic acid	15.0	50	0	0
2	acetic acid	15.3	231	40	76
3	acetol	16.1	106	6	16
4	acrylic acid	18.7	21	1	1
5	furfural	19.2	6	90	73
6	2-furanmethanol	19.8	26	2	9

[a] Expressed as chromatographic peak areas per mole of starting sugar.

Table 2. Formation Efficiencies[a] ($\times 10^{12}$) of Selected Pyrolysis Products of gl1p, gl6p, and gl on a DB-1 Capillary Column

	name	t_R (min)	gl1p	gl6p	gl
1	formic acid	7.6	73	6	0
2	acetic acid	8.0	145	12	0.7
3	furfural	8.7	4	36	5.0
4	acetylformoin	11.8	1	10	0.1
5	Furaneol	13.3	3	8	0.1
6	pyranone	14.5	2	9	0.2
7	hydroxymethylfurfural	15.5	0	7	0.4

[a] Expressed as chromatographic peak areas per mole of starting sugar.

substances to more aroma and color generation. The ability to control relative amounts of different intermediates formed will be desirable to limit or enhance the formation of specific products stemming from these precursors or intermediates. To elucidate the role of specific phosphorylation in controlling the thermal decomposition of glucose and its effect on the direction of Maillard reaction, glucose-1-phosphate and glucose-6-phosphate were subjected to Py/GC/MS analysis in the absence and presence of ammonium carbonate, glycine, and cysteine hydrochloride. The model systems were analyzed using nonpolar PLOT and medium polar DB-1 columns. In general, the phosphate sugars produced more volatiles both in numbers and in amounts. For example, the pyrolysis of glucose on the PLOT column (**Figure 1**) produced only eight peaks: acetaldehyde, 2,3-butanedione, hydroxy-acetaldehyde, acetic acid, 1-hydroxy-2-propanone, furfural, 2-furanmethanol, and 1-(2-furanyl)-ethanone, while the pyrolysis of glucose-1-phophate and glucose-6-phophate produced 29 and 22 compounds, respectively (see **Figures 1** and **2** and **Tables 1** and **2**). It seems that phosphorylation increases sugar degradation and enhances the further reactivity of the phosphorylated intermediates such as 1- and 3-deoxyglucosones. In general, the physical and chemical properties of reducing sugars are strongly affected by the relative concentrations of different tautomeric forms. Specifically, the concentration of the open chain forms greatly influences the rate of chemical reactions including thermal decompositions to produce sugar fragments. It has been demonstrated that glucose-6-phophate and ribose-5-phosphate had a much higher concentration of open chain form than their nonphosphorylated counterparts (*14*). It is expected therefore that higher intensities and numbers of products generated from phosphorylated sugars will be observed since thermal decompositions are usually initiated from open forms of reducing sugars.

Thermal Decomposition of Glucose-1-phosphate in the Presence and Absence of Amino Acids. Examination of thermal decomposition products of glucose-1-phosphate alone (see **Tables 1** and **2** and **Figures 1** and **2**) indicated significant increases in the intensities of the degradation products of the sugar that can arise from its open form, such as formic acid, acetic acid, and 1-hydroxy-2-propanone (acetol). Consistent with this observation, glucose-1-phosphate, heated in the presence of glycine, also produced significantly higher amounts of pyrazines (see **Tables 3** and **4** and **Figures 3** and **4**). Pyrazines are known to require sugar fragments that arise from its open form for their formation. For example, the area of trimethylpyrazine increased 9-fold relative to unphosphorylated glucose per mole of the starting sugar (on PLOT-Q column). In the presence of ammonium carbonate, the amount of acetic acid

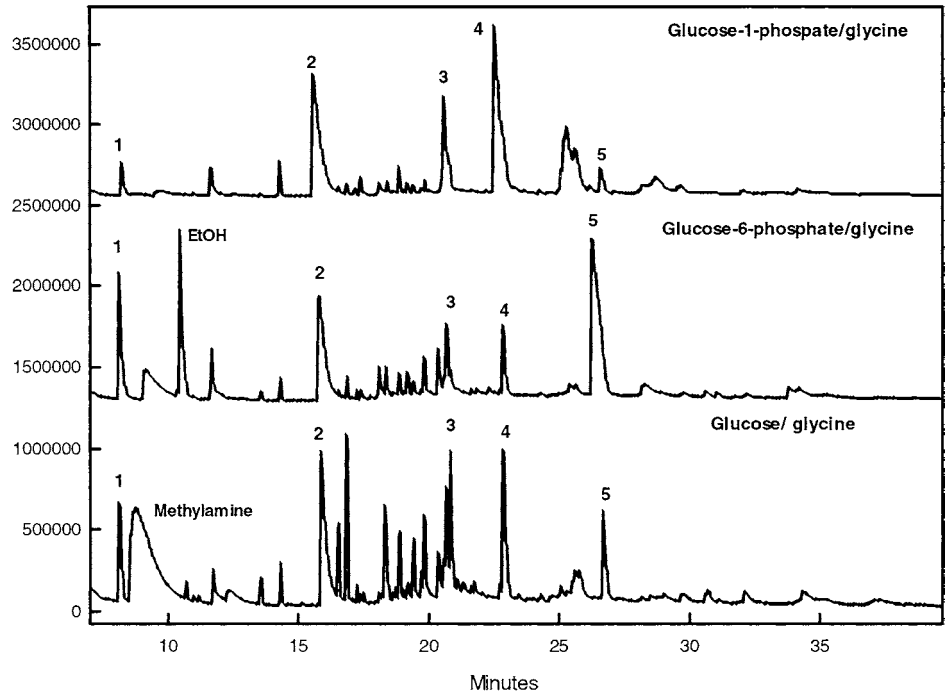


Figure 3. Chromatograms of pyrolysis of glucose, glucose-1-phosphate, and glucose-6-phosphate in the presence of glycine on a PLOT-Q capillary column. Key: 1, 2-amino-1-propanol; 2, acetic acid; 3, 2,5-dimethylpyrazine; 4, trimethylpyrazine; 5, 2-acetylpyrrole.

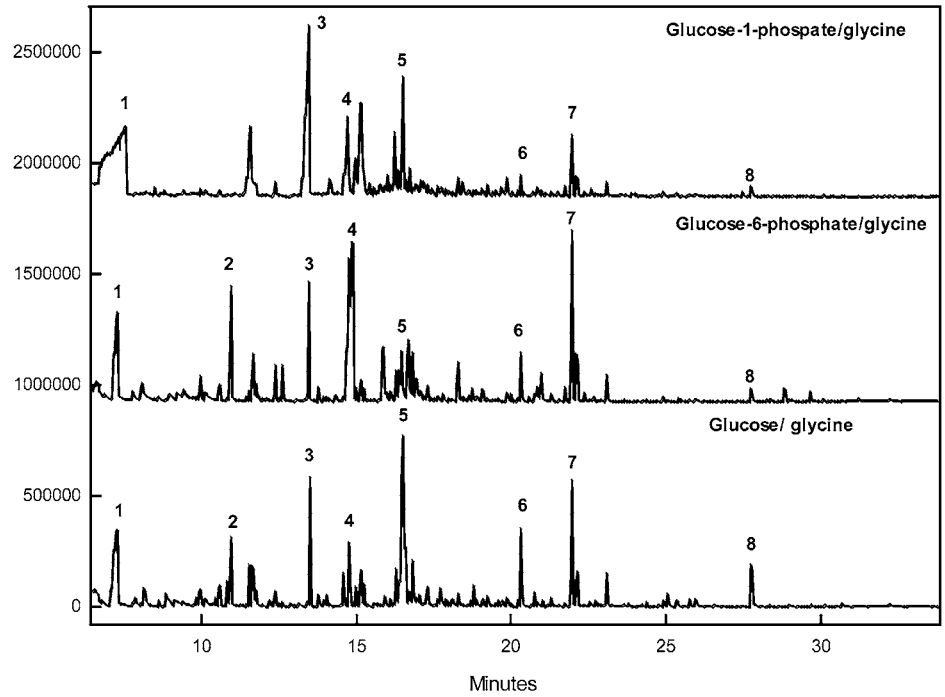


Figure 4. Chromatograms of pyrolysis of glucose, glucose-1-phosphate, and glucose-6-phosphate in the presence of glycine on a DB-1 capillary column. Key: 1, acetic acid; 2, 4-cyclopentene-1,3-dione; 3, trimethylpyrazine; 4, 4-hydroxy-2,5-dimethyl-3-(2H)-furanone (Furaneol); 5, pyranone; 6, dimethyl pyrazinone; 7, trimethyl pyrazinone; 8, quinoxalinone.

increased 4-fold and that of 2,3-butanedione increased 2-fold relative to glucose (see **Table 5** and **Figure 5**). However, in the presence of cysteine hydrochloride, no significant changes in the intensities of the reaction products were observed due to the hydrolysis of the phosphate groups by the action of the released acid (see **Table 6** and **Figure 6**). The effect of glucose-1-phosphate on the product distribution during the Maillard reaction can be rationalized by the phosphate-assisted ring opening of the sugar and hence increased concentration of reactive intermediates (see **Scheme 1**) present during the reaction.

Thermal Decomposition of Glucose-6-phosphate in the Presence and Absence of Amino Acids. Contrary to the effect induced by C-1 phosphorylation on the product distribution, examination of thermal decomposition products of glucose-6-phosphatealone (see **Tables 1** and **2** and **Figures 1** and **2**)

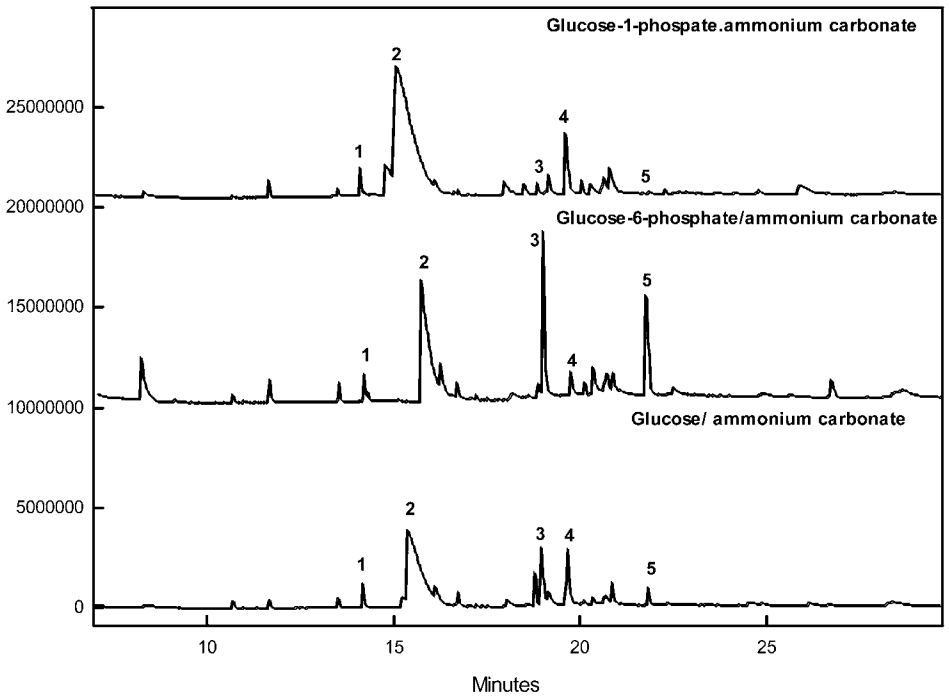


Figure 5. Chromatograms of pyrolysis of glucose, glucose-1-phosphate, and glucose-6-phosphate in the presence of ammonium carbonate on a PLOT-Q capillary column. Key: 1, 2,3-butanedione; 2, acetic acid; 3, furfural; 4, 2-furanmethanol; 5, 5-methylfurfural.

Table 3. Formation Efficiencies[a] ($\times 10^{12}$) of Selected Pyrolysis Products of gl1p, gl6p, and gl in the Presence of Glycine (gc) on a PLOT-Q Capillary Column

	name	t_R (min)	gl1p/gc	gl6p/gc	gl/gc
1	2-amino-1-propanol	8.0	5	13	4
2	acetic acid	15.8	72	26	18
3	2,5-dimethylpyrazine	20.7	27	4	6
	2-acetylfuran	20.8	1	1	3
	5-methylfurfural	21.8	0	0.05	trace
4	trimethylpyrazine	22.8	86	9	10
5	2-acetylpyrrole	26.6	7	45	6

[a] Expressed as chromatographic peak areas per mole of starting sugar.

Table 4. Formation Efficiencies[a] ($\times 10^{9}$) of Selected Pyrolysis Products of gl1p, gl6p, and gl in the Presence of gc on a DB-5 Capillary Column

	name	t_R (min)	gl1p/gc	gl6p/gc	gl/gc
1	acetic acid	7.2	38	8	7
2	4-cyclopentene-1,3-dione	10.9	0	3	2
	2-acetylfuran	11.5	0.1	0.2	1
	5-methylfurfural	12.6	0	6.0	1
3	trimethylpyrazine	13.4	21	03	3
4	Furaneol	14.7	3	6	1
	2-acetylpyrrole	14.8	0.6	10	1
5	pyranone	16.5	0.4	1	13
6	dimethylpyrazinone	20.3	0.1	1	2
7	trimethylpyrazinone	21.9	0.2	4	4
8	quinoxalinone	27.8	0.3	0.2	0.8

[a] Expressed as chromatographic peak areas per mole of starting sugar.

indicated significant increases in the intensities of products formed from relatively intact sugars such as 1,6-dimethyl-2,4-dihydroxy-3(2H)furanone (acetylformoin), Furaneol, 5-hydroxymethylfurfural (HMF), furfural, and 4-cyclopentene-1,3-dione, except the relative intensities of 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one (pyranone) and 2-acetylfuran both containing six sugar carbons diminished significantly (see **Scheme 2**). Consistent with this observation, glucose-6-phosphate, heated in the presence of glycine, also produced significantly higher amounts of 2-acetylpyrrole, 5-methylfurfural, Furaneol, and 4-cyclopentene-1,3-dione. On the other hand, the relative intensities of 2,3-dihydro-3,5-dihydroxy-6-

Table 5. Formation Efficiencies[a] ($\times 10^{12}$) of Selected Pyrolysis Products of gl1p, gl6p, and gl in the Presence of Ammonium Carbonate (ac) on a PLOT-Q Capillary Column

	name	t_R (min)	gl1p/ac	gl6p/ac	gl/ac
1	2,3-butanedione	14.1	18	4	9
2	acetic acid	15.0	712	83	171
3	furfural	19.0	9	40	28
4	2-furanmethanol	19.6	62	5	31
5	5-methylfurfural	21.8	3	24	8

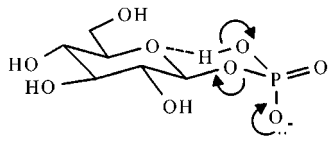
[a] Expressed as chromatographic peak areas per mole of starting sugar.

Table 6. Formation Efficiencies[a] ($\times 10^{12}$) of Selected Pyrolysis Products gl1p, gl6p, and gl in the Presence of Cysteine Hydrochloride (cs) on a PLOT-Q Capillary Column

	name	t_R (min)	gl1p/cs	gl6p/cs	gl/cs
1	acetaldehyde	8.2	47	59	58
2	ethylene sulfide	12.0	25	26	38
3	2-methylfuran	13.6	15	28	26
4	2-butanone	14.4	5	4	9
5	thiophene	15.1	76	84	93
6	thiazole	16.9	57	60	42
7	2-methylthiazole	18.6	14	14	16
8	2-acetylfuran	21.0	25	15	45
9	5-ethyl-2-methylthiazole	23.8	40	23	33

[a] Expressed as chromatographic peak areas per mole of starting sugar.

Scheme 1. Phosphate-Assisted Ring Opening of Glucose-1-phosphate



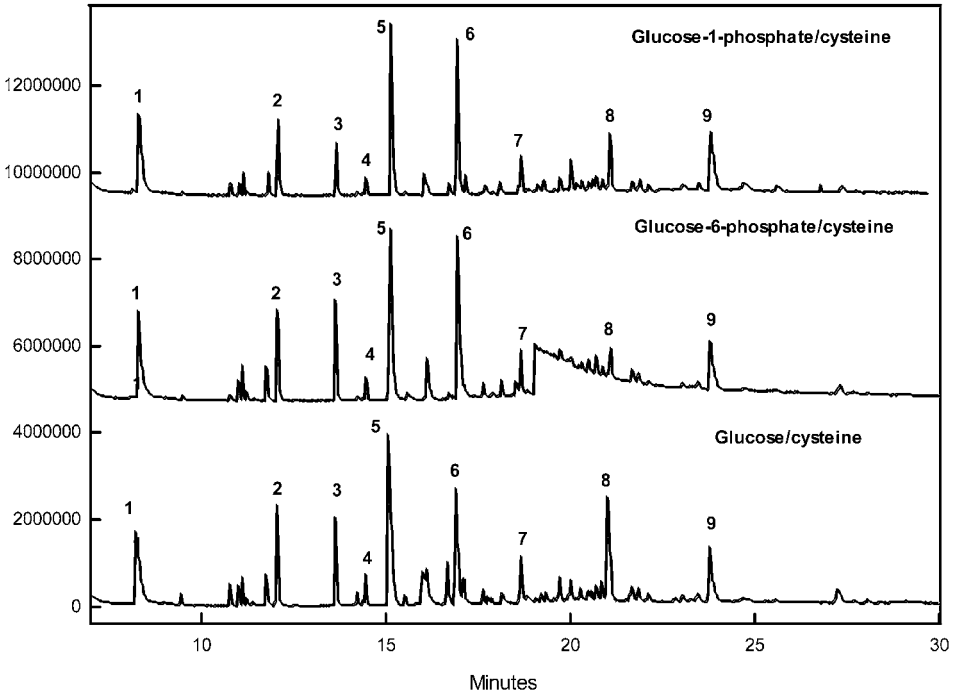


Figure 6. Chromatograms of pyrolysis of glucose, glucose-1-phosphate, and glucose-6-phosphate in the presence of cysteine hydrochloride on a PLOT-Q capillary column. Key: 1, acetaldehyde; 2, ethylene sulfide; 3, 2-methylfuran; 4, 2-butanone; 5, thiophene; 6, thiazole; 7, 2-methylthiazole; 8, 1-(2-furanyl)ethanone; 9, 5-ethyl-2-methylthiazole.

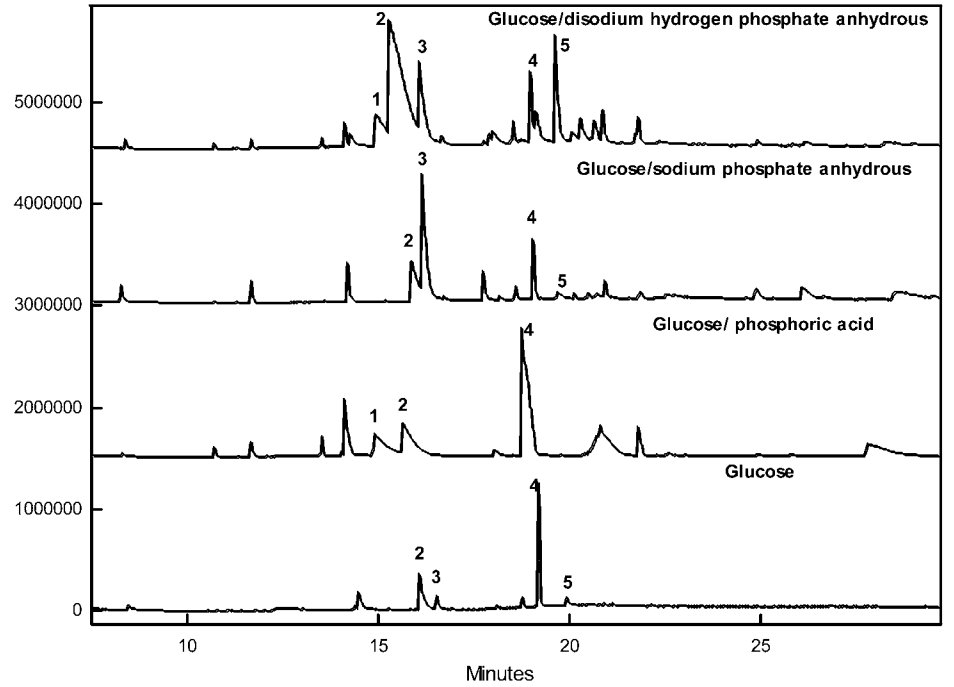
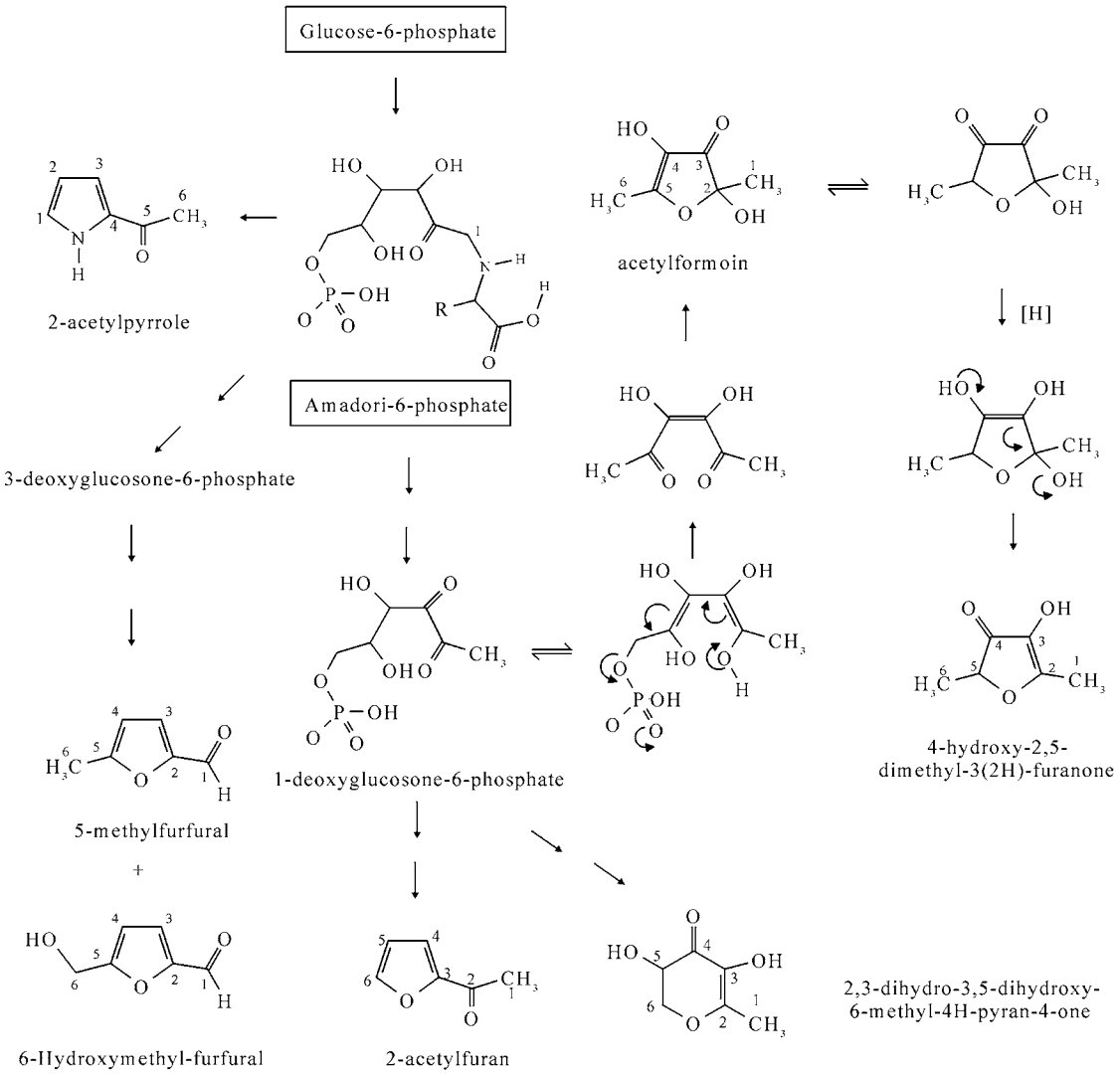


Figure 7. Chromatograms of pyrolysis of glucose in the presence of various phosphate salts and phosphoric acid on a PLOT-Q capillary column. Key: 1, formic acid; 2, acetic acid; 3, acetol; 4, furfural; 5, 2-furanmethanol.

methyl-4H-pyran-4-one and 2-acetylfuran were also diminished significantly (see **Tables 3** and **4** and **Figures 3** and **4**). In the presence of ammonium carbonate, the amount of 5-methylfurfural increased 3-fold and that of furfural increased around 2-fold relative to glucose (see **Table 5** and **Figure 5**). However, in the presence of cysteine hydrochloride, no significant changes in the intensities of the reaction products were observed due to the hydrolysis of the phosphate groups by the action of the released acid (see **Table 6** and **Figure 6**).

The role that glucose-6-phosphate plays in the Maillard reaction and observed above can be rationalized by three distinct processes: (i) The presence of a phosphate group inhibits generation of Maillard products formed by nucleophilic action initiated by the C-6 hydroxyl group by blocking the nucleophilic atom, such as during formation of 2-acetylfuran and 2,3-dihydro-3,5-dihydroxy-4H-pyran-4-one (see **Scheme 2**). The involvement of the C-6 hydroxyl group as the nucleophilic moiety has been confirmed previously by ^{13}C-labeling studies (*3*, *15*). In

Scheme 2. Role of Glucose-6-phosphate in the Formation of 6-Deoxy-glucose Derivatives 1,6-Dimethyl-2,4-dihydroxy-3-(2H)-furanone (Acetylformoin), 2-Acetylpyrrole, 5-Methylfurfural, 2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one, 4-Hydroxy-2,5-dimethyl-3-(2H)-furanone (Furaneol), and HMF[a]

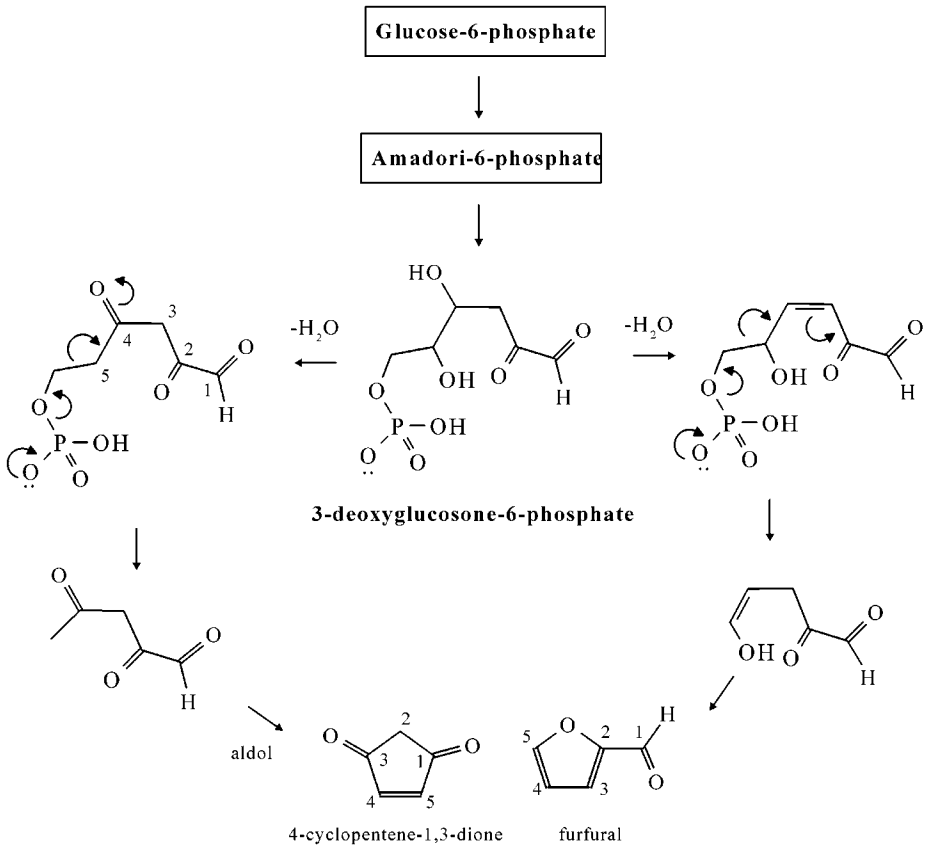


[a] Numbers indicate original glucose carbon positions based on *J. Agric. Food Chem.* **2000**, *48*, 2451–2418.

the presence of glycine, 2-acetylfuran formation diminished by 4-fold and that of 2,3-dihydro-3,5-dihydroxy-4H-pyran-4-one diminished by around 13-fold (see **Table 4**). (ii) The phosphate group, being a good leaving group, enhances the generation of Maillard products formed by the elimination of the C-6 hydroxyl group such as in the formation of acetylformoin, 2-acetylpyrrole, 5-methylfurfural, and Furaneol. **Scheme 2** illustrates the mechanism of formation of an important intermediate in the Maillard reaction, acetylformoin (*16*), as an example of the importance of leaving group ability of the C-6 hydroxyl group in the formation of Maillard products. This compound was detected in trace amounts in the glucose model system, but it was one of the major peaks in the glucose-6-phosphate model system (see **Figure 2** and **Table 2**). Because hydroxyl groups are not good leaving groups, they have to be protonated or phosphorylated to generate elimination products mentioned earlier and summarized in **Scheme 2**. **Table 4** also indicates around a 5-fold increase in 2-acetylpyrrole and a 6-fold increase in 5-methylfurfural and Furaneol relative to unphosphorylated glucose model system. (iii) The presence of a phosphate group can also stabilize and hence increase the half-life of the anionic species such as 1- and 3-deoxyglucoson-6-phosphate anions (see **Schemes 2** and **3**) through resonance and therefore increase the concentrations of products derived directly from them, such as HMF, which increased by 18-fold relative to the glucose model system (see **Table 2**). In addition, retro-aldol reactions initiated from C-6 hydroxyl groups are also enhanced as shown in **Scheme 3** due to the same factor. The amount of 4-cyclopentene-1,3-dione almost doubled in the glycine model system (**Table 4**) and that of furfural increased by 7-fold as shown in **Table 2**.

Effect of Free Phosphates on the Thermal Decomposition of Glucose in the Presence and Absence of Amino Acids. Specifically phosphorylated sugars such as glucose-1- and 6-phosphates are relatively costly to use; therefore, we have also studied the role of excess (4-fold) free phosphates, such as sodium phosphate dibasic, sodium phosphate monobasic, and phosphoric acid, in controlling the Maillard reaction (see **Table 7** and **Figure 7**). It appeared that sodium phosphate dibasic was the most efficient reagent in initiating sugar degradations as was evidenced by a 23-fold increase in the total formation efficiencies of the five compounds listed in **Table 7**. In effect, addition of sodium phosphate dibasic produced a strikingly similar profile to that of glucose-1-phosphate (see **Figure 1**). This can be explained by the ability of phosphate ions to catalyze sugar ring opening through simultaneous proton donation and

Scheme 3. Role of Glucose-6-phosphate in Enhancing Retro-Aldol Reactions and Formation of Furfural and 4-Cyclopentene-1,3-dione[a]



[a] Numbers indicate original glucose carbon positions based on *J. Agric. Food Chem*. **2000**, *48*, 2451–2418.

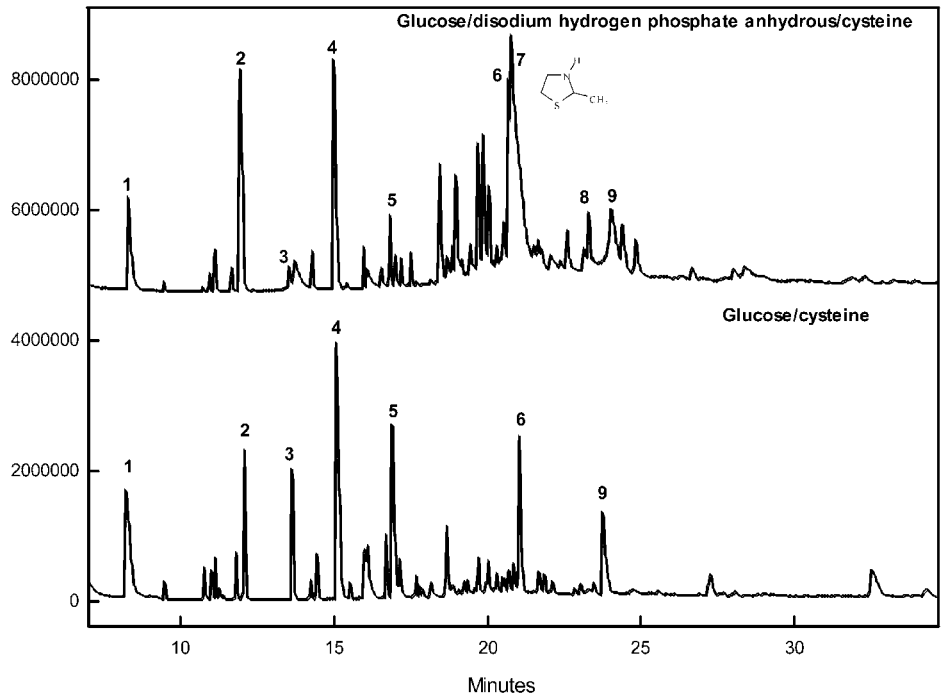


Figure 8. Chromatograms of pyrolysis of glucose/cysteine model system in the presence and absence of disodium hydrogen phosphate on a PLOT-Q capillary column. Key: 1, acetaldehyde; 2, ethylene sulfide; 3, 2-methylfuran; 4, thiophene; 5, thiazole; 6, 1-(2-furanyl)ethanone; 7, 2-methylthiazolidine; 8, 5-ethyl-2-methylthiazole; 9, 4-ethyl-5-methylthiazole.

abstraction as shown in **Scheme 4a**, in a fashion similar to that of glucose-1-phosphate. In addition, when glucose/dibasic phosphate mixture was pyrolyzed in the presence of cysteine, it promoted the formation of 2-methylthiazolidine, 4-ethyl-2-methylthiazole, and 4-ethyl-5-methylthiazole (see **Table 8** and **Figure 8**). In fact, the first two were only formed in the presence of dibasic phosphate and 2-methylthiazolidine was the most abundant peak in the chromatogram. It has been proposed that

Table 7. Formation Efficiencies[a] ($\times 10^{12}$) of Selected Pyrolysis Products of gl in the Presence of Various Phosphate Salts and Phosphoric Acid on a PLOT-Q Capillary Column

	name	t_R (min)	gl/Na_2HPO_4	gl/NaH_2PO_4	gl/H_3PO_4	gl
1	formic acid	14.7	382	3	92	0
2	acetic acid	15.6	2870	26	71	76
3	acetol	16.3	756	6	0	16
4	furfural	18.7	233	106	257	93
5	2-furanmethanol	19.7	638	7	0	9

[a] Expressed as chromatographic peak areas per mole of starting sugar.

Scheme 4. Intramolecular Proton Exchange Can Facilitate Phosphate-Assisted (a) Ring Opening of Glucose and (b) Decarboxylation of Amino Acids

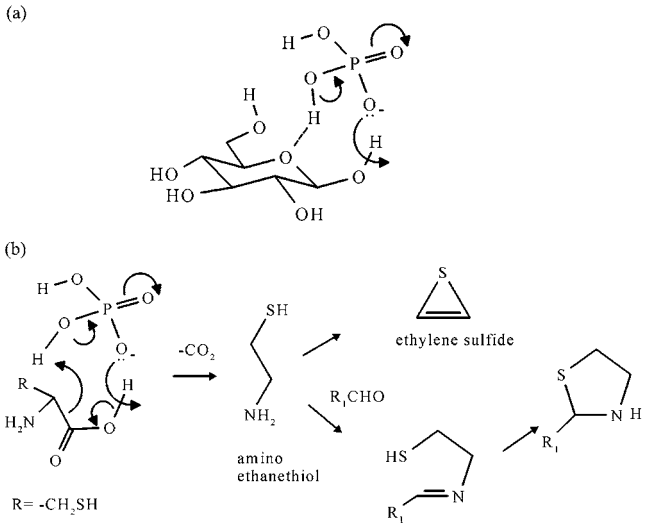


Table 8. Formation Efficiencies[a] ($\times 10^{12}$) of Selected Pyrolysis Products of the gl/cs Model System in the Presence and Absence of Disodium Hydrogen Phosphate on a PLOT-Q Capillary Column

	name	t_R (min)	gl/Na_2HPO_4/cs	gl/cs
1	acetaldehyde	8.2	36	58
2	ethylene sulfide	12.0	63	38
3	2-methylfuran	13.6	5	26
4	thiophene	15.1	60	93
5	thiazole	16.9	12	42
6	2-acetylfuran	20.7	32	45
7	2-methylthiazolidine	20.8	231	0
8	5-ethyl-2-methylthiazole	23.3	21	0
9	4-ethyl-5-methylthiazole	24.4	71	33

[a] Expressed as chromatographic peak areas per mole of starting sugar.

thiazolidines can be formed by the interaction of amino-ethanethiol (decarboxylated cysteine) with carbonyl compounds such as acetaldehyde and glyoxal (*17*). Increased efficiency of formation of ethylene sulfide along with 2-methylthiazolidine (see **Table 8**) indicates the ability of phosphate ions to also catalyze decarboxylation of amino acids in a fashion similar to its catalysis of ring opening of sugars, as shown in **Scheme 4b**. According to this scheme, increased concentrations of amino-ethanethiol can explain increased efficiency of formation of both ethyene sulfide and 2-methylthiazolidine. A similar role has been also ascribed to the phosphate ions by de Kok and Rosing (*18*).

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